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REVISION

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# High Density Heterogenisation of Molecular Electrocatalysts in a Rigid Intrinsically Microporous Polymer Host

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## **Abstract**

A water-insoluble Polymer with Intrinsic Microporosity (or PIM, here for the particular case of the Tröger Base system PIM-EA-TB, BET area ca.  $10^3 \text{ m}^2\text{g}^{-1}$ ) is demonstrated to act as a rigid host environment for highly water-insoluble molecular catalysts, here tetraphenylporphyrinato-iron (FeTPP), surrounded by aqueous solution-filled micropores. A PIM-EA-TB film containing catalyst is deposited onto the electrode and immersed for voltammetry (i) with 4-(3-phenyl-propyl)-pyridine to give an organogel, or (ii) bare directly into aqueous solution. The porous host allows processes to be optimised as a function of solution phase, composition, and catalyst loading. Effective electron transfer as well as effective electrocatalysis is reported for aqueous oxygen and peroxide reduction. Given the use of completely water-insoluble catalyst systems, the methodology offers potential for application with a wide range of hitherto unexplored molecular electrocatalysts and catalyst combinations in aqueous media.

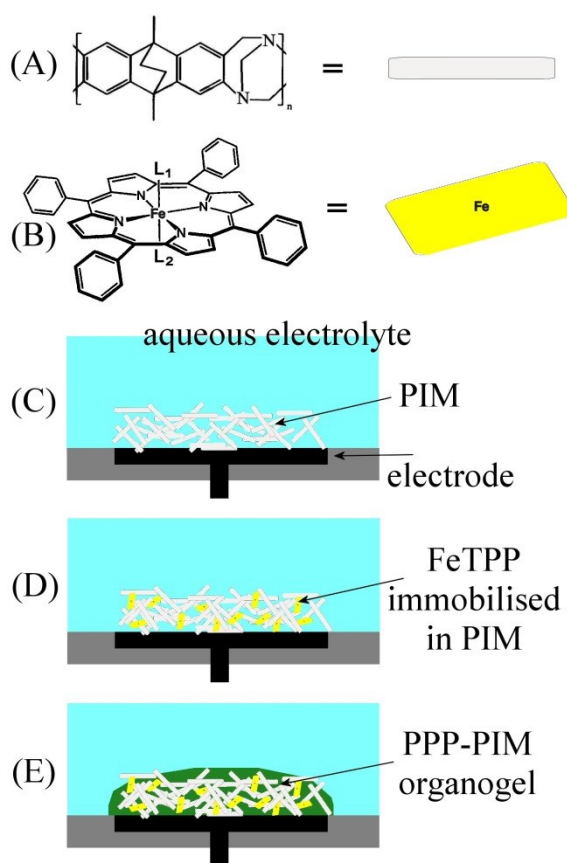
**Keywords:** electrocatalysis, ion transfer, peroxide, oxygen,  $\text{CO}_2$ , fuel cell, membrane, sensing.

## 1. Introduction

High density heterogenisation of molecular catalysts and/or catalyst systems is desirable (i) to exploit the benefits of assembled molecular catalysts at electrode surfaces, (ii) to avoid catalyst losses due to dissolution and separation, (iii) to enable “families” or “ensembles” of catalysts and co-catalysts to be assembled into active films, and (iv) to allow screening of catalyst activity as a function of solvent system, electrolyte, ionic strength, or pH. Most commonly applied are direct surface immobilisation strategies based on adsorption of catalysts,<sup>1,2</sup> electrostatic attachment,<sup>3</sup> or covalent attachment via carbon<sup>4</sup> or ethynyl<sup>5</sup> bonds. These methods require suitable surfaces, high surface area, and carefully executed surface chemistry. An alternative strategy can be based on porous host materials such as conducting polymers,<sup>6</sup> network polymers,<sup>7</sup> zeolites,<sup>8</sup> intercalation materials,<sup>9</sup> sol-gels,<sup>10</sup> which in turn need to be immobilised or pasted<sup>11</sup> into the electrode material. In particular gels and polymer hosts are beneficial and readily applied, although stability of these host materials, aging, cross-linking, and non-rigidity causing mobility of guest species can be problematic.

Recently, a novel family of highly rigid and therefore highly intrinsically microporous polymer (PIM) materials has been proposed.<sup>12,13</sup> In dry gas media these porous polymers allow gas separation<sup>14</sup> and gas storage.<sup>15</sup> When immersed in electrolyte media and in

particular when carrying intrinsic charge (e.g. the poly-amine PIM-EA-TB when protonated, see Figure 1A<sup>16</sup>), these rigid and microporous polymer materials become desirable for applications in electrochemistry.<sup>17,18</sup>



**Figure 1.** (A) Molecular structure of PIM-EA-TB. (B) Molecular structure of FeTPP. Schematic drawings of (C) PIM immobilised onto an electrode, (D) with FeTPP immobilised into the rigid microporous structure, and (E) with PPP to form a separate organogel phase.

In this report, it is demonstrated that the microporous PIM-EA-TB offers an ideal rigid (suppressing Ostwald ripening) environment for molecular catalysts, such as the water-insoluble model system FeTPP (see Figure 1B). Figure 1D represents a schematic depiction

of the case of molecular FeTPP catalyst randomly distributed within the rigid host and surrounded by aqueous electrolyte. Figure 1E depicts the case of a water-immiscible organic solvent, here 4-(3-phenyl-propyl)-pyridine or PPP,<sup>19</sup> co-deposited into the porous PIM-EA-TB host to give an organogel, which is used here to characterise the chemically reversible one-electron transformation Fe(II/III)TPP (with coordination of PPP in L<sub>1</sub> and L<sub>2</sub> position, Figure 1B) coupled to anion transfer from the aqueous phase. The aqueous system (Figure 1D) is demonstrated for the electrocatalytic reduction of oxygen and of hydrogen peroxide.

## **2. Experimental**

### **2.1. Chemical Reagents**

4-(3-phenylpropyl)-pyridine (97%), 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron(III) chloride (FeTPP<sub>2</sub>Cl), phosphoric acid (85%wt), sodium hydroxide (>97%), dimethylformamide (HPLC grade, >99.9%), NaClO<sub>4</sub>, NaPF<sub>6</sub>, NaNO<sub>3</sub>, hydrogen peroxide (35%wt) were obtained from Aldrich or Fisher Scientific. PIM-EA-TB was prepared following a literature recipe.<sup>16</sup> Solutions were prepared with filtered and deionized water of resistivity 18.2 MΩ cm from a Thermo Scientific water purification system.

### **2.2. Instrumentation**

A potentiostat system (IVIUM Compactstat) was employed with a Pt wire counter electrode and a KCl-saturated calomel reference (SCE, Radiometer, Denmark). The working electrode was a glassy carbon electrode (3 mm diameter, BAS). The UV/Vis

experiments were performed with a Varian UV-Visible spectrophotometer. All experiments were conducted at a temperature of  $293 \pm 2\text{K}$ .

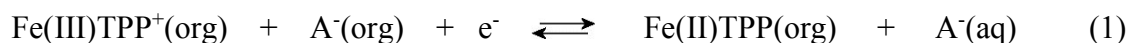
### 2.3. Procedures for Electrode Preparation

Solution A of PIM-EA-TB ( $1\text{ mg cm}^{-3}$ ) in dimethylformamide (DMF) acidified with  $5\text{ }\mu\text{L}$   $\text{HClO}_4$  was prepared. Solution B of  $\text{FeTPP}\text{Cl}$  ( $1\text{ mg cm}^{-3}$ ) in DMF solution was prepared. Then solution A and B were mixed and  $1\text{ }\mu\text{L}$  mixture deposited onto the glassy carbon electrode surface with solvent evaporation at  $90\text{ }^\circ\text{C}$  in an oven. A free-standing membrane 1:1  $\text{FeTPP}\text{Cl}$ :PIM was prepared by solution evaporation in a Teflon mould (see Figure 2B). Films deposited onto glass slides were characterised by UV/Vis (Figure 2A) and the characteristic Soret band at  $414\text{ nm}^{20}$  is observed.

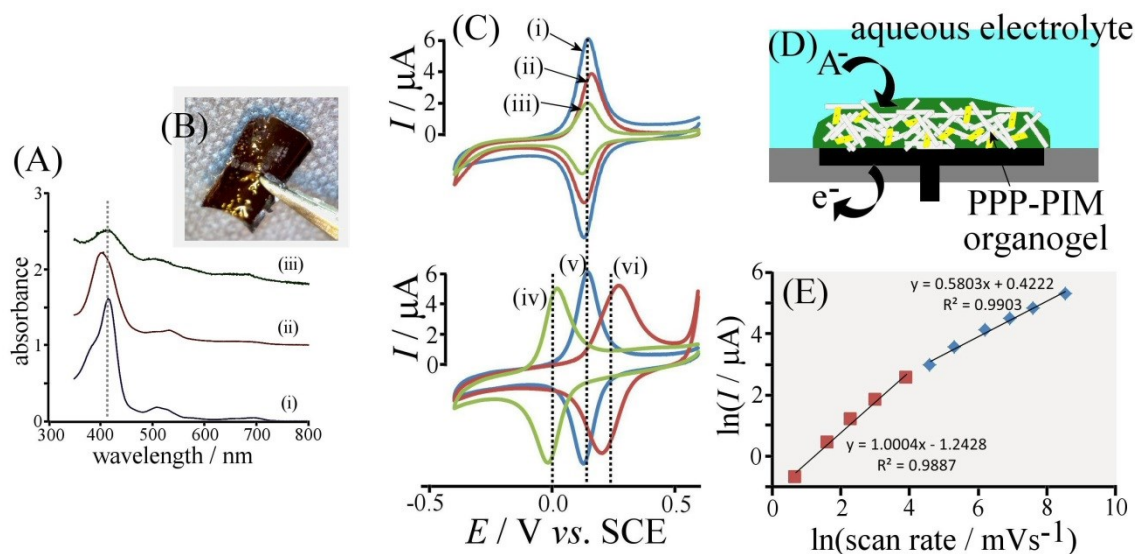
## 3. Results and Discussion

### 3.1. PIM-Catalyst Films I.: Voltammetry of $\text{FeTPP}$ in Organogel Environments

In order to investigate the immobilised  $\text{FeTPP}$  redox system initially the organic solvent 4-(3-phenyl-propyl)-pyridine or PPP is applied to the  $\text{FeTPP}$ -PIM film to give a water-immiscible organogel film (see Figure 2D). The axial positions  $\text{L}_1$  and  $\text{L}_2$  (see Figure 1B) are likely to be occupied by the pyridine-derivative solvent giving chemically reversible one-electron character to the  $\text{Fe(III/II)TPP}$  redox system<sup>21</sup> (equation 1).



The anion  $A^-(aq)$  here is the perchlorate anion, which is transferred between organic and aqueous phase with a midpoint potential of 0.145 V vs. SCE consistent with literature reports.<sup>26</sup> By varying the type of anion from  $PF_6^-$  to  $ClO_4^-$  to  $NO_3^-$  a characteristic sequence of midpoint potentials is observed (Figure 2Civ-vi) due to the variation in anion transfer potential.<sup>26</sup>



**Figure 2.** (A) UV/Vis spectra for (i)  $0.1 \text{ mg cm}^{-3}$  FeTPP in DMF, (ii) a film of 1:5 FeTPP:PIM, and (iii) a film of 5:1 FeTPP:PIM (ii and iii are offset for clarity). (B) Photograph of a free-standing PIM-TeTPP membrane. (C) Cyclic voltammograms (scan rate  $20 \text{ mVs}^{-1}$ ) for the oxidation of FeTPP immobilised into PIM and coated with PPP (to give an organogel phase separate from the aqueous phase) immersed in 0.1 M phosphate buffer pH 7 with 0.1 M  $NaClO_4$  for FeTPP:PIM weight ratios (i) 1:1, (ii) 1:5, (iii) 1:20. Also shown are data for 1:1 FeTPP:PIM immersed in phosphate buffer with (iv) 0.1 M  $NaPF_6$ , (v) 0.1 M  $NaClO_4$ , and (vi)  $NaNO_3$ . (D) Schematic drawing of the liquid|liquid anion transfer process coupled to the  $FeTPP^{+/0}$  redox process at the electrode surface. (E) Plot (double logarithmic) of the peak current for the oxidation of FeTPP:PIM 1:1 in phosphate buffer with 0.1 M  $NaClO_4$  as a function of scan rate.

When varying the FeTPP:PIM film composition from 1:1 to 1:5 to 1:20 (by weight) the peak current for both oxidation and back-reduction changes accordingly (Figure 2Ci-iii).



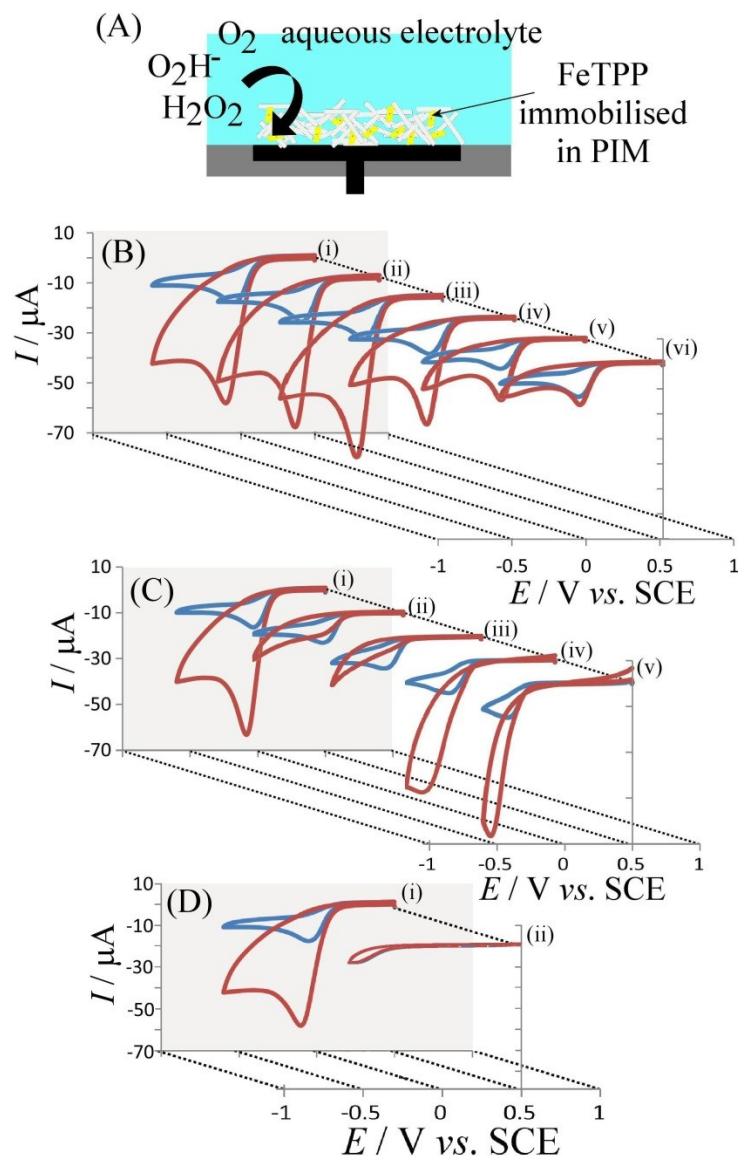
The effect of scan rate is investigated for FeTPP:PIM 1:1 as shown in Figure 2E. At lower scan rates up to ca. 50 mVs<sup>-1</sup> an approximately linear increase in peak current with scan rate is indicative of a nearly complete electrolysis of the FeTPP contained in the film (thin film case; the charge under the peak, ca. 30  $\mu$ C, is consistent with the amount of deposit). At higher scan rates approximately square root dependence of peak current versus scan rate is indicative of diffusion (thick film case). Overall, an active organogel film containing FeTPP-PIM surrounded by solvent is demonstrated.

### 3.2. PIM-Catalyst Films II.: Voltammetry of FeTPP in Aqueous Environments

The molecular catalyst FeTPP and derivatives thereof have biomimetic significance and have been employed previously in oxidation chemistry as well as in the electrocatalytic reduction of O<sub>2</sub> and CO<sub>2</sub>.<sup>22</sup> When immobilised in the form of the FeTPP-PIM film and immersed into aqueous 0.1 M phosphate buffer pH 2, there is no direct electrochemical response to be attributed to the FeTPP catalyst. However, the catalytic reduction of oxygen (ca. 0.18 mM ambient concentration<sup>23</sup>) is readily detected at -0.044 V vs. SCE with a peak current of -17  $\mu$ A (see Figure 3B). In contrast, at bare glassy carbon or PIM-EA-TB coated glassy carbon, this reduction peak is shifted more negative by ca. 0.4 V and is reduced in peak current (Figure 3D). The peak current in the presence of catalyst can be compared to the value estimated by the Randles-Sevcik equation<sup>24</sup> (equation 2).

$$I_{peak} = 2.69 \times 10^5 n^{3/2} AD^{1/2} cv^{1/2} \approx 16 \mu A \quad (2)$$

In this equation the diffusion controlled peak current  $I_{peak}$  is expressed in terms of  $n$ , the number of electrons transferred per molecule diffusing to the electrode surface,  $A = 7.1 \times 10^{-6} \text{ m}^2$ , the geometric electrode area,  $D = 1.65 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ ,<sup>28</sup> the diffusion coefficient for oxygen,  $c = 0.18 \text{ mM}$ , the ambient concentration of oxygen, and  $\nu$ , the scan rate. The agreement is good and a four-electron reduction appears likely. When adding  $\text{H}_2\text{O}_2$  into the solution to give a 4 mM concentration, the cathodic current increases accordingly (Figure 4Bi), consistent with catalytic reduction of  $\text{H}_2\text{O}_2$  to water at the potential of oxygen reduction.



**Figure 3.** (A) Schematic drawing of the FeTPP-PIM film coated electrode immersed in aqueous electrolyte with hydrogen peroxide neutral or as mono-anions. (B) Cyclic voltammograms (scan rate  $20 \text{ mVs}^{-1}$ ) for the reduction of ambient oxygen (blue) and  $4 \text{ mM } H_2O_2$  (red) at electrodes coated with (i) 1:1, (ii) 1:2, (iii) 1:5, (iv) 1:10, (v) 1:20, and (vi) 1:40 weight ratio FeTPP:PIM immersed in aqueous  $0.1 \text{ M}$  phosphate buffer pH 2. (C) Cyclic voltammograms (scan rate  $20 \text{ mVs}^{-1}$ ) for the reduction of ambient oxygen (blue) and  $4 \text{ mM } H_2O_2$  (red) at electrodes coated with 1:5 FeTPP:PIM immersed in aqueous  $0.1 \text{ M}$  phosphate buffer at pH (i) 2, (ii) 4, (iii) 7, (iv) 9, and (v) 12. (D) As above at pH 2 showing (i) 1:5 FeTPP:PIM and (ii) bare glassy carbon.

When changing the FeTPP:PIM ratio, the cathodic response for the reduction of oxygen remains approximately constant (with a decrease in peak current to ca. 10  $\mu\text{A}$ ), however, the reduction of  $\text{H}_2\text{O}_2$  is suppressed at 1:10 weight ratio. Therefore, a high concentration of FeTPP in PIM is necessary for the reduction of  $\text{H}_2\text{O}_2$  to water, but not for the reduction of oxygen to  $\text{H}_2\text{O}_2$ , indicative of two mechanisms.

When changing the pH of the solution, significant changes in catalytic activity are observed (see Figure 3C for FeTPP:PIM 1:5). For the oxygen reduction only a shift in peak potential (ca. 40 mV per pH unit) is observed with the peak current remaining approximately constant (i.e. the electrocatalytic reduction remains a four-electron process). However, the reduction of  $\text{H}_2\text{O}_2$  is suppressed at pH 4 and pH 7 and then re-emerges at pH 9. These changes are likely to be linked to (i) the presence of reaction intermediates, (ii) the inter-catalyst site distance, (iii) disproportionation/dismutation processes, as well as (iv) charge transport within the film and require further study.

#### **4. Conclusion**

It has been shown that a highly water-insoluble molecular electrocatalyst, FeTPP $\text{Cl}$ , is readily immobilised in a rigid microporous PIM-EA-TB polymer film. Electrochemical activity is demonstrated in the presence of an organic solvent (with PPP as water-insoluble organic phase liquid-liquid anion transfer coupled to electron transfer is observed) and electrocatalytic activity is demonstrated in aqueous electrolyte media. Four-electron reduction of oxygen and two-electron reduction of hydrogen peroxide occur at a similar

potential with both (i) the density of electrocatalyst in the polymer matrix and (ii) the pH playing a crucial role in making the catalytic reaction effective.

In future, a broader range of PIM-hosts for electrocatalysts could be developed specifically for application in sensing and/or in fuel cell catalysis. High density co-immobilisation of several catalysts and co-catalysts in layers or nano-structures (mimicking bio-films) will allow reactions to be controlled and/or coupled effectively.

### **Acknowledgement**

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